

2.(a) Electrical Properties of Materials

Syllabus

Classical free electron theory - Expression for electrical conductivity - Thermal conductivity, expression - Wiedemann-Franz law - Success and failures – Quantum free electron theory: Tunnelling - Degenerate states - Fermi- Dirac statistics - Density of energy states - Electron effective mass - Concept of hole.

Objectives

- ❖ Understanding about the conduction properties of metals.
- ❖ Knowledge on various theories of electrons in solids.
- ❖ Knowledge on the different factors, affecting the conductivity of metals and the energy of electrons in metals.
- ❖ Proper Knowledge on the distribution and concentration and emission o electrons.
- ❖ Understanding about the variation of Fermi level with temperature and concentration of impurities in semiconductors.

Keywords: Conducting materials, Free electrons, Classical free electron theory, Zone theory, Drift velocity (v_d), Relaxation time (τ), Collision time (τ_c), Mean free path (λ), Electrical conductivity, Thermal Conductivity (K), Wiedemann – Franz law, Lorentz Number, Fermi distribution function, Density of Energy States.

1. Introduction

Materials with low resistance are generally called as **conducting materials**. These materials have higher electrical and thermal conductivities. They conduct a large quantity of heat and electricity.

This conducting property of a material depends only on the number of **valence electrons** (electrons in the outermost orbit) available and not on the total number of electrons in the metal. These valence electrons are also called as **free electrons (or) conducting electrons**.

Classification of solids into Conductors, Semiconductors and Insulators

On the basis of forbidden band Conductors, Semiconductors and Insulators are described as follows:

1. Conductors

In case of conductors, there is no forbidden band and the valence band and conduction band overlap each other. Here, plenty of free electrons are available for electric conduction. The electrons from valence band freely enter in the conduction band. The most important point in conductors is that due to the absence of forbidden band, there is no structure to establish holes. The total current in conductors is simply a flow of electrons.

2. Semi-Conductors

In semiconductors, the forbidden band is very small. Germanium and silicon are the examples of semiconductors. In Germanium the forbidden band is of the order of 0.7eV while in case of silicon, the forbidden gap is of the order of 1.1eV. Actually, a semi-conductor material is one whose electrical properties lie between insulators and good conductors. At 0°K, there are no electrons in conduction band and the valence band is completely filled.

When a small amount of energy is supplied, the electrons can easily jump from valence band to conduction band. For example, when the temperature is increased, the forbidden band is decreased so that some electrons are liberated into the conduction band. In semi-conductors, the conductivities are of the order of 10^2 ohm-metre.

3. Insulators

In case of insulators, the forbidden energy band is wide. Due to this fact, electrons cannot jump from valence band to conduction band. In insulators, the valence electrons are bound very tightly to their parent atoms.

For example, in case of materials like glass, the valence band is completely filled at 0K and the energy gap between valence band and conduction band is of the order of 10 eV. Even in the presence of high electric field, the electrons do not move from valence band to conduction band. When a very large energy is supplied, an electron may be able to jump across the forbidden gap. Increase in temperature enables some electrons to go to the conduction band. **This explains why certain materials which are insulator become conductors at high temperature.** The resistivity of insulators is of the order of 10^7 ohm-metre.

1.1 Electron Theory of Metals

The electron theory of solids explains the structures and properties of solids through their electronic structure. This theory is applicable to all solids both metals and non-metals. This theory also explains the binding in solids, behavior of conductors and insulators,

Ferromagnetism, electrical and thermal conductivities of solids, elasticity, cohesive and repulsive forces in solids etc., the theory has been developed in three main stages.

Main stages of electron theory of solids

i) Classical free electron theory

In 1900, Drude and Lorentz developed this theory. According to this theory, **the metals contain free electrons and these free electrons are responsible for the electrical conduction in the metals.** This theory obeys the laws of classical mechanics. In this theory, the free electrons in metals are assumed to move in a constant potential.

ii) Quantum free electron theory

Sommerfield developed this theory during 1928, in which the free electrons obey the quantum laws. According to this theory, the electrons in a metal move in a constant potential and it obeys the laws of quantum mechanics.

iii) Zone theory (or) band theory of solids

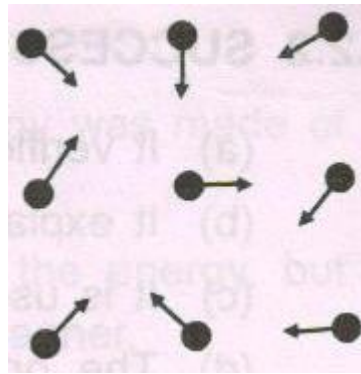
Bloch stated this theory in 1928. According to this theory, **the free electrons move in a periodic potential provided by the periodicity of the crystal lattice.** Since this theory explains the electrical conductivity based on the energy bands it is also called as Band theory of solids.

Classical Free electron theory of metals

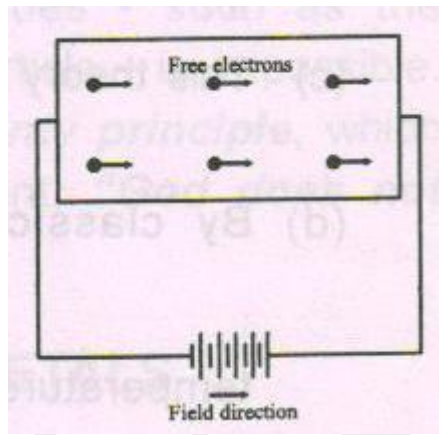
Postulates:

The classical electron theory is based on the following postulates:

- i) A solid metal consists of atoms and atoms have nucleus around which electrons are revolving.
- ii) The valence electrons of atoms in a metal are free to move about the whole volume of the metal like the molecules of a perfect gas in a container. Thus in classical free electron theory, one visualizes the collection of valence electrons from all the atoms forming an electron gas which is free to move throughout the volume of the metal.
- iii) **In the absence of electric field**, these free electrons move in random directions and collide with either positive ions fixed to the lattice or other free electrons. All these collisions are elastic i.e., there is no loss of energy.



- iv) **When an electric field is applied to the metal**, the free electrons are accelerated in the direction opposite to the direction of applied electric field. Since the electrons are assumed to be a perfect gas molecule, they obey classical kinetic theory of gases.



- v) The electron velocities in metal obey the classical maxwell-Boltzmann distribution of velocities.
- vi) **Drift velocity (v_d):** It is defined as the average velocity acquired by the free electron in a particular direction due to the application of electric field.
- vii) **Relaxation time (τ):** It is the time taken by the free electron to reach its equilibrium position from its disturbed position in the presence of applied field.
- viii) **Collision time (τ_c):** It is the average time taken by a free electron between two successive collisions.
- ix) **Mean free path (λ):** The average distance traveled between two successive collisions is called mean free path.

1.2 Electrical conductivity of a metal

Let us consider a conductor of unit volume and ‘n’ be the number of free electrons in it. In the absence of an electric field, these free electrons will move in different directions with different velocities. The average velocity of the electrons at any instant in any direction must be zero.

When an electric field is applied to the conductor, the electrons are subjected to acceleration. The drift velocity of the electrons will depend upon the applied field, greater is the drift velocity

and consequently, higher would be the number of electrons per second through unit area, i.e., the current passing through the conductor will be high.

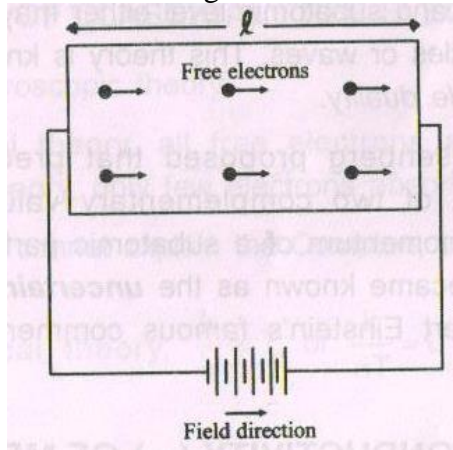
The force experienced by an electron $F = eE$

(1)

Where,

E – Applied electric field

e – The electronic charge



When an electric field (E) is applied between the two ends of a metallic rod. The electrons will move in opposite direction to the applied external field with a drift velocity V_d

$$\text{Acceleration (a)} = \frac{V_d}{\tau} \tag{1}$$

Where V_d – drift velocity; τ – Relaxation Time

If ‘ E ’ is the electric field applied on an electron of charge ‘ e ’, then

$$\text{Force acting on the electron, } F = eE \tag{2}$$

Where F is a driving force

$$\text{From newton II law of motion, Force on the electron, } F = \text{mass (m) x acceleration (a)} \tag{3}$$

$$\text{Sub. (1) in (3), we get } F = \frac{mV_d}{\tau} \tag{4}$$

$$\text{From equations (2) \& (4) } eE = \frac{mV_d}{\tau} \text{ (or) } V_d = \left(\frac{e\tau}{m}\right)E \tag{5}$$

From ohm’s law, the current density (J) is expressed in terms of electrical conductivity (σ) as

$$J = \sigma E \text{ (or) } \sigma = \frac{J}{E} \tag{6}$$

Also, the current density in terms of drift velocity can be written as $J = neV_d$

$$\text{Sub. (5) in (7), we get } J = ne\left(\frac{e\tau}{m}\right)E \text{ (or) } \frac{J}{E} = \frac{ne^2\tau}{m} \tag{8}$$

$$\text{i.e., Electrical conductivity } \sigma = \frac{ne^2\tau}{m} \tag{9}$$

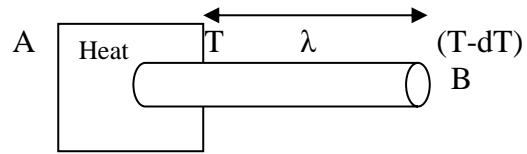
Thus, the amount of electric charge (Q) conducted per unit time (t) across unit area (A) of the solid per unit applied electrical field (E).is called electrical conductivity

$$\sigma = \frac{q}{tAE}$$

Thermal Conductivity:

“It is defined as the amount of heat (Q) flowing per unit time through the material having unit area of cross section and maintaining at unit temperature gradient (dT/dx)”

$$\text{i.e., } Q = K \frac{dT}{dx} \quad (\text{or}) \quad K = \frac{Q}{\frac{dT}{dx}} \quad (10)$$



Consider two cross sections ‘A’ at high temperature (T) & ‘B’ at low temperature (T-dT) in a uniform metallic rod ‘AB’. Two cross sections ‘A’ and ‘B’ are separated by a distance ‘λ’. The conduction of heat takes place from ‘A’ to ‘B’ through electrons. During collision, electrons near ‘A’ lose their kinetic energy while electrons near ‘B’ gains the energy

Let the density of conduction electron be ‘n’ and velocity of electron be ‘v’.

$$\text{At ‘A’ average kinetic energy of the electron} = \frac{3}{2}kT \quad \therefore K.E = \left[\frac{1}{2}mv^2 = \frac{3}{2}kT \right] \quad (11)$$

Where k – Boltzmann Constant and T – absolute temperature

$$\text{At ‘B’ average kinetic energy of the electron} = \frac{3}{2}k(T-dT) \quad (12)$$

(12)

$$\therefore \text{Excess Kinetic energy from A to B of an electron} = \frac{3}{2}kT - \frac{3}{2}k(T-dT) = \frac{3}{2}kdT \quad (13)$$

(13)

$$\text{Number of electrons crossing unit area per unit time from ‘A’ to ‘B’} = \frac{1}{6}nv \quad (14)$$

(14)

$$\text{Excess energy carried from ‘A’ to ‘B’ for unit area in unit time} = \frac{1}{6}nv \times \frac{3}{2}kdT = \frac{1}{4}nvkdT \quad (15)$$

(15)

$$\text{III}^{\text{ly}}, \text{Deficient energy carried from ‘B’ to ‘A’ for unit area in unit time} = -\frac{1}{4}nvkdT \quad (16)$$

$$\text{Net amount energy transferred from ‘A’ to ‘B’} \quad Q = \frac{1}{4}nvkdT - \left(-\frac{1}{4}nvkdT\right)$$

$$\text{(or)} \quad Q = \frac{1}{2}nvkdT \quad (17)$$

$$\text{But, by definition } Q = K \frac{dT}{dx} \quad (\text{or}) \quad Q = K \frac{dT}{\lambda}$$

$$\therefore K = \frac{1}{2}nvk\lambda \quad (18)$$

W.K.T for metals, relaxation time (τ) = Collision time (τ_c).

$$\text{i.e., } \tau = \tau_c = \frac{\lambda}{v} \quad (\text{or}) \quad \tau v = \lambda \quad (19)$$

$$\text{Sub. Eqn (19) in (18), we get } \therefore K = \frac{1}{2}nv^2k\tau \quad (20)$$

This is the Expression for Thermal Conductivity

Wiedemann – Franz Law:

$$\text{Dividing equation (20) by (9), we get, } \frac{\text{Thermal Conductivity}}{\text{Electrical Conductivity}} = \frac{K}{\sigma} = \frac{\frac{1}{2}nv^2k\tau}{\frac{ne^2\tau}{m}}$$

$$\text{(or)} \quad \frac{K}{\sigma} = \frac{1}{2} \frac{mv^2k}{e^2} \quad (21)$$

$$\text{W.K.T the kinetic energy of an electron is } \frac{1}{2}mv^2 = \frac{3}{2}kT$$

Then, equation (21) becomes $\frac{K}{\sigma} = \frac{3}{2} \times \frac{kT \times k}{e^2} = \frac{3}{2} \left(\frac{k^2}{e^2} \right) T$

$$\text{(or) } \boxed{\frac{K}{\sigma} = LT}$$

Where $L = \frac{3}{2} \left(\frac{k^2}{e^2} \right)$ is a constant called Lorentz number. By substituting the value of

$$k = 1.38 \times 10^{-23} \text{JK}^{-1}, e = 1.6 \times 10^{-19} \text{Coulomb}, L = 1.12 \times 10^{-8} \text{W}\Omega\text{K}^{-1}. \boxed{\frac{K}{\sigma} \propto T}$$

Thus “The ratio of thermal conductivity to electrical conductivity of a metal is directly proportional to absolute temperature of the metal”

Lorentz Number

Lorentz number is a constant given by

$$L = \frac{3}{2} \left(\frac{K_B}{e} \right)^2$$

$$K_B = 1.38 \times 10^{-23} \text{JK}^{-1}$$

$$e = 1.6021 \times 10^{-19} \text{Coulomb}$$

$$\therefore L = \frac{3}{2} \left(\frac{1.38 \times 10^{-23}}{1.6021 \times 10^{-19}} \right)^2 = 1.12 \times 10^{-8} \text{W}\Omega\text{K}^{-2}$$

$$\text{i.e., } L = 1.12 \times 10^{-8} \text{W}\Omega\text{K}^{-2}$$

where,

It is found that the classical value of lorentz number is only half of the experimental value i.e.,

$$L = 2.24 \times 10^{-8} \text{W}\Omega\text{K}^{-2}$$

This discrepancy in the experimental and theoretical value of lorentz number is the failure of classical theory. This discrepancy is rectified by quantum theory.

Success of classical free electron theory

- (i) It verifies Ohm’s law
- (ii) It explains the electrical and thermal conductivities of metals.
- (iii) It derives Wiedemann – Franz law.
- (iv) It explains optical properties of metals.

1.5 Drawbacks of Classical Free electron Theory

- (i) From the classical free electron theory the value of specific heat of metals is given by $4.5 R$, where R is called the universal gas constant. But experimental value of specific heat is nearly equal to $3R$. Further according to classical free electron theory, the value of the electronic specific heat is equal to $3/2R$. But actually it is about $0.01 R$ only.

- (ii) By classical free electron theory, the Lorentz number is given by

$$L = \frac{3}{2} \left(\frac{K_B}{e} \right)^2 = \frac{3}{2} \left(\frac{1.38 \times 10^{-23}}{1.602 \times 10^{-19}} \right)^2$$
$$= 1.12 \times 10^{-8} W \Omega K^{-2}$$

For copper at 20°C, the electrical resistivity is 1.72×10^{-8} ohm-m and the thermal conductivity is 386 w/m/k. Hence,

$$L = \frac{K}{\sigma T} = \frac{k\rho}{T} = 2.26 \times 10^{-8} W \Omega K^{-2}$$

This value does not agree with the calculated value based on the classical free electron theory. Thus it suggests that all the free electrons in a metal do not participate in thermal conduction and electrical conduction as assumed by the classical free electron theory.

- (iii) Electrical conductivity of semiconductors or insulators could not be explained using this theory
- (iv) The theoretical value of paramagnetic susceptibility is greater than the experimental value. Ferromagnetic cannot be explained by this theory.
- (v) The photo electric effect, Compton effect and black body radiation cannot be explained by the classical free electron theory.

QUANTUM FREE ELECTRON THEORY

The failures of classical theory were rectified in quantum theory given by Sommerfield in the year 1928. This theory uses quantum concepts such as Schrodinger wave equation and de-Broglie concept of matter waves to obtain the expression for electron energies.

Postulates:

The potential energy of an electron is uniform or constant within the metal.

The electrons have wave nature.

The allowed energy levels of an electron are quantized

The electrons move freely within the metal and they are not allowed to leave the metal due to existence of potential barrier at its surfaces

The free electrons obey Fermi-Dirac statistics.

Merits

This theory treats the electron quantum mechanically rather than classically.

It explains the electrical conductivity, thermal conductivity, specific heat capacity of metals, photoelectric effect, Compton effect, etc.,

Demerits

Even though it explains most of the physical properties of the metals, it fails to state the difference between conductor, semiconductor and insulator.

It also fails to explain the positive value of Hall coefficient and some of the transport properties of the metals.

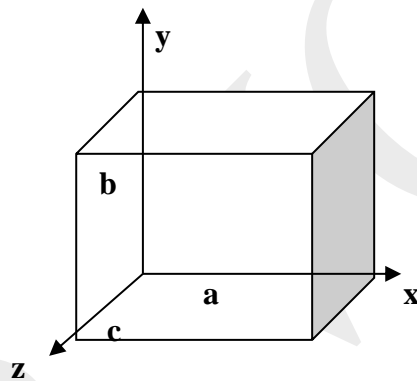
Electrons in metals – Particle in three-dimensional box

The Solution of one-dimensional potential box can be extended for a three-dimensional potential box. Here the particle can move in any direction in space. Hence instead of one quantum number ‘n’ three quantum numbers n_x, n_y, n_z are considered corresponding to the three coordinating axis (x,y,z)

Three-dimensional potential box.

If a,b,c, are the length of the box as shown in figure along x,y,z axis ,then the energy of the particle $E_n = E_x + E_y + E_z$

$$\text{i.e., } E_{n_x, n_y, n_z} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$



For a perfect cubic box $a = b = c$

$$\text{Energy Eigen value is } E_{n_x, n_y, n_z} = \frac{h^2}{8m} [n_x^2 + n_y^2 + n_z^2] \tag{1}$$

The corresponding normalized wave function of an electron in a cubical box can be rewritten as

$$\psi_{n_x, n_y, n_z} = \sqrt{\frac{2}{a}} \times \sqrt{\frac{2}{a}} \times \sqrt{\frac{2}{a}} \cdot \sin \frac{n_x \pi x}{a} \cdot \sin \frac{n_y \pi y}{a} \cdot \sin \frac{n_z \pi z}{a} \tag{2}$$

Degeneracy:

It is nothing but the set of quantum numbers having same Eigen value but different Eigen function. Such states and energy levels are called *Degenerate state*

Eg : if a state of quantum numbers are

$$\begin{aligned} n_x = 1 ; n_y = 2 ; \quad n_z = 1, n_x = 1 ; n_y = 1 ; n_z = 2 \text{ \&} \\ n_x = 2 ; n_y = 1 ; \quad n_z = 1 \text{ have same Eigen values as } n_x^2 + n_y^2 + n_z^2 = 6 \end{aligned}$$

$$E_{121} = E_{112} = E_{211} = \frac{6h^2}{8ma^2} \tag{3}$$

But the corresponding Eigen functions are

$$\left. \begin{aligned} \psi_{121} &= \sqrt{\frac{8}{a^3}} \cdot \sin \frac{\pi x}{a} \cdot \sin \frac{2\pi y}{a} \cdot \sin \frac{\pi z}{a} \\ \psi_{112} &= \sqrt{\frac{8}{a^3}} \cdot \sin \frac{\pi x}{a} \cdot \sin \frac{\pi y}{a} \cdot \sin \frac{2\pi z}{a} \\ \psi_{211} &= \sqrt{\frac{8}{a^3}} \cdot \sin \frac{2\pi x}{a} \cdot \sin \frac{\pi y}{a} \cdot \sin \frac{\pi z}{a} \end{aligned} \right\} \tag{4}$$

Non - Degeneracy:

For various combinations of quantum numbers if we have same energy Eigen value and Eigen function then each state and energy levels are called *Non – degenerate state*

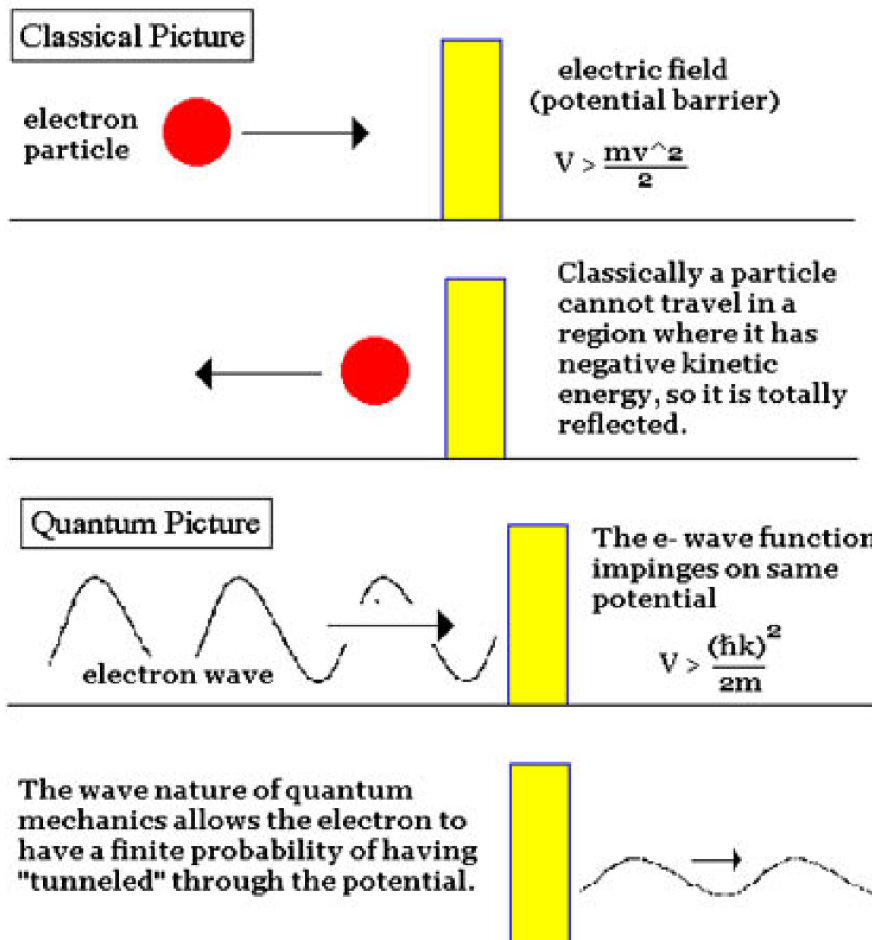
Eg : for $n_x = 2 ; n_y = 2 ; n_z = 2$ we have $E_{222} = \frac{12h^2}{8ma^2}$ &

$$\psi_{222} = \sqrt{\frac{8}{a^3}} \cdot \sin \frac{2\pi x}{a} \cdot \sin \frac{2\pi y}{a} \cdot \sin \frac{2\pi z}{a}$$

Barrier penetration and quantum tunneling (Qualitative)

- According to classical ideas, a particle striking a hard wall has no chance of leaking through it. But, the behaviour of a quantum particle is different due to the wave nature associated with it.
- We know that when an electromagnetic wave strikes at the interface of two media, it is partly reflected and partly transmitted through the interface and enters the second medium.
- In a similar way the de Broglie wave also has a possibility of getting partly reflected from the boundary of the potential well and partly penetrating through the barrier.
- Figure shows a particle with energy $E < V$ approaching potential barrier of height V .
- An electron of total energy E approaches the barrier from the left. From the view point of classical physics, the electron would be reflected from the barrier because its energy E is less than V .
- For the particle to overcome the potential barrier, it must have an energy equal to or greater than V .

Quantum mechanics leads to an entirely new result. It shows that there is a finite chance for the electron to leak to the other side of the barrier. It is noted that the electron tunnelled through the potential barrier and hence in quantum mechanics, this phenomenon is called tunneling. The transmission of electrons through the barrier is known as barrier penetration.



Expression for Transmission Probability

- Now let us consider the case of a particle of energy $E < V$ approaching a potential barrier of finite height and width as shown in figure.
- The particle in region I has certain probability of passing through the barrier to reach region II and then emerge out on the other side in region III.
- The particle lacks the energy to go over the top of the barrier, but tunnels through it. Higher the barrier and wider it is, the lesser is the probability of the particle tunneling through it.
- Let us now consider a beam of identical particles, all having kinetic energy E . The beam is incident on the potential barrier of height V and width a from height I.
- On both sides of the barrier $V = 0$, This means that no forces act on particles in regions I and III.
- Here, the wave function ψ_1 represents the particle moving towards the barrier from region I while ψ_2 represents the particle reflected moving away from the barrier.
- The wave function ψ_3 represents the particle inside the barrier. Some of the particles end up in the region III while the other return to region I.
- Quantum mechanics shows that the transmission probability T for a particle to pass

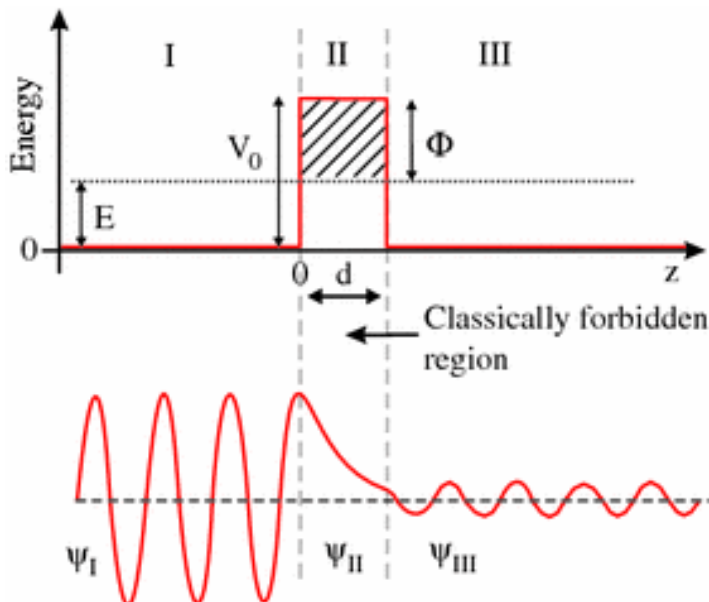
$$T = \frac{\text{Number of particles transmitted}}{\text{Number of particles incident}}$$

through the barrier is given by

This is approximately given by $T = T_0 e^{-2ka}$

$$k = \frac{\sqrt{2m(V - E)}}{h}$$

Where h and a is the width of the barrier. T_0 is a constant close to unity. It shows that the probability of particle penetration through a potential barrier depends on the height and width of the barrier.



Significance

Tunneling is a very important physical phenomena which occurs in certain semiconductor diodes. In such diodes electrons pass through potential barriers even though their kinetic energies are smaller than the barrier heights.

The tunneling effect also occurs in the case of the alpha particles. The kinetic energy of alpha particle is only a few MeV but it is able to escape from a nucleus whose potential wall is perhaps 25 MeV high.

The ability of electrons to tunnel through a potential barrier is used in the Scanning Tunneling Microscope (STM) to study surfaces on an atomic scale of size.

Electron energies in metals and Fermi energy

Fermi Dirac Statistics

In metals, the electrons are distributed among the different possible energy states. **In a metal, the energy of the highest filled state at 0K is called the Fermi energy E_F or Fermi level.** The magnitude of E_F depends on how many free electrons there are. At 0K all states upto E_F are occupied and states above E_F are empty.

The probability $F(E)$ of an electron occupying a given energy level is known as Fermi-Dirac distribution function and it is written as

$$F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{K_B T}\right)}$$

Where, $F(E)$ = Fermi Function

E = Energy of the level whose occupancy is being considered.

E_F = Fermi energy of the system

K_B = Boltzmann's constant

T = Absolute temperature

The probability value of $F(E)$ lies between 0 and 1

Unit probability means that the state is always full. Zero probability means that it is always empty.

At temperatures above 0K some electrons absorb thermal energy and move into higher quantum states. The Pauli Exclusion Principle rules that an electron can only enter an empty state, so that thermally excited ones must go into states above E_F .

Thermodynamics shows that the average allowance of thermal energy to a particle in a system at a temperature T K is of the order kT so that only electron within an energy interval kT from E_F can take up thermal energy and go to higher states with energy $E_F + kT$. At room temperature kT is only $10^{-2} E_F$ or less, so that only something like 1% of the electrons can take their allowance. That's why the specific heat of the electron gas is much smaller than what the classical free electron theory predicts.

Variation of Fermi-Dirac distribution function with temperature:

At 0 Kelvin the electrons filled all the states up to a certain maximum energy level (E_{max}), called **Fermi level** or **Fermi energy**. The Fermi level is a boundary line which separates all the filled states and empty states. At 0K all states up to E_F are filled and states above E_F are empty.

Case 1: At 0K

(i) If $E > E_F$,

$$F(E) = \frac{1}{1 + e^{\infty}} = \frac{1}{\infty} = 0$$

$$\therefore F(E) = 0$$

(ii) If $E < E_F$

$$F(E) = \frac{1}{1 + e^{-\infty}} = \frac{1}{1} = 1$$

$$\therefore F(E) = 1$$

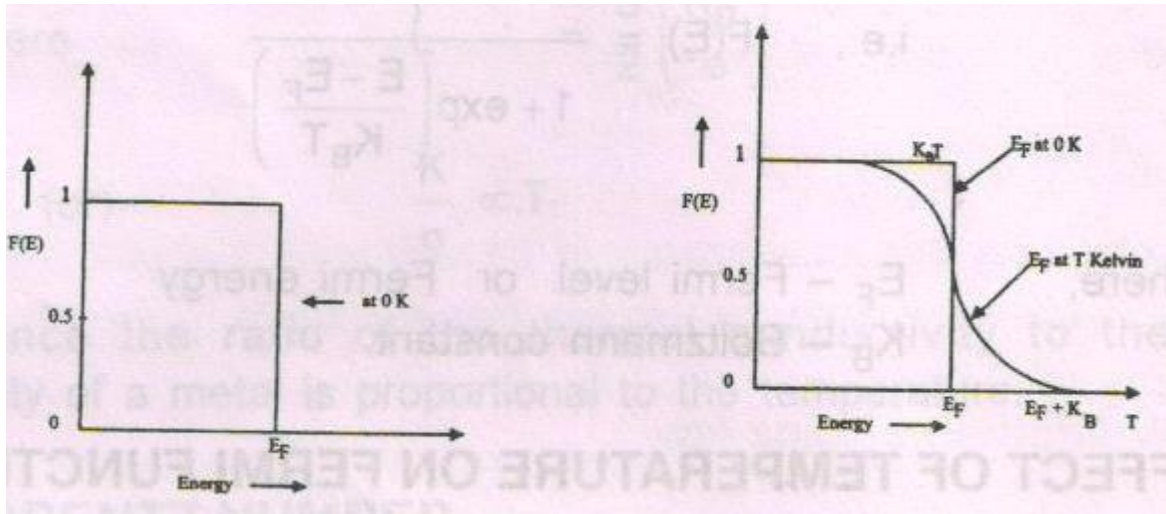
ie, Fermi function is 100%. It means 100% chance for the electron to be filled within the Fermi level.

(iii) If $E = E_F$

$$F(E) = \frac{1}{1 + 1} = \frac{1}{2} = 0.5$$

$$\therefore F(E) = 0.5$$

ie, Fermi function is 50%. It means 50% chance for the electron to be filled within the Fermi level.



Density of Energy States and Carrier Concentration in Metals

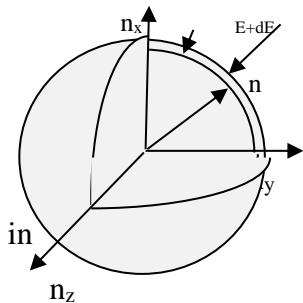
Definition:

Density of states is defined as the number of energy states present in an energy interval dE (the energy range from E to $(E+dE)$ per unit volume of the material.

E

Density of States:

Let us consider a cubical sample with side 'a' as length. A sphere is constructed with quantum numbers n_x, n_y, n_z as three coordinate axes in three dimensional space.



A radius vector 'n' is drawn from the origin 'O' to a point with set of quantum number n_x, n_y, n_z . In space have same energy 'E'. Thus, $n^2 = n_x^2 + n_y^2 + n_z^2$ denotes the radius of the sphere with energy 'E'. This shell is further divided into number of sub shells with particular number in particular energy state which is having particular radius vector

Number of energy states within a sphere of radius 'n' = $\frac{4}{3} \pi n^3$

(1)

Since the quantum number n_x, n_y, n_z have only +ve integer value, we have to take only one octant of sphere $\left(\frac{1}{8}\right)$

\therefore No. of available energy states within one octant of sphere of radius 'n' } $= \frac{1}{8} \times \left[\frac{4}{3} \pi n^3 \right]$ (2)
 Corresponding to energy 'E' }

III^{ly} No. of available energy states within one octant of sphere of radius 'n+dn' corresponding to energy 'E+dE' } = $\frac{1}{8} \times \left[\frac{4}{3} \pi (n+dn)^3 \right]$ (3)

No. of available energy states between the shell of radius 'n' & 'n+dn'

$$= \frac{1}{8} \times \left[\left[\frac{4}{3} \pi (n+dn)^3 \right] - \left[\frac{4}{3} \pi n^3 \right] \right]$$

$$= \frac{1}{8} \times \frac{4\pi}{3} \left([n+dn]^3 - n^3 \right)$$

$$\therefore N(E) = \frac{1}{8} \times \frac{4\pi}{3} (n^3 + dn^3 + 3n^2dn + 3ndn^2 - n^3)$$

Neglecting higher power of dn which is very small, N (E) dE = $\frac{1}{8} \times \left[\frac{4}{3} 3n^2dn \right]$ (or)

$$N(E) dE = \left[\frac{\pi}{2} n^2 dn \right] \quad \text{(or)} \quad N(E) dE = \left[\frac{\pi}{2} n(ndn) \right] \quad (4)$$

We know that, the particle in a one dimensional box of radius 'a' in Schrödinger's wave equation is

$$E = \frac{n^2 h^2}{8ma^2} \quad (5)$$

$$\text{(or)} \quad n^2 = \frac{8ma^2 E}{h^2} \quad (6)$$

$$\text{(or)} \quad n = \left[\frac{8ma^2 E}{h^2} \right]^{\frac{1}{2}} \quad (7)$$

$$\text{Differentiating eqn (6) w.r.t } n \text{ \& } E, \text{ we get } 2ndn = \frac{8ma^2}{h^2} dE \quad (8)$$

$$\text{(or)} \quad ndn = \frac{8ma^2}{2h^2} dE \quad (9)$$

Sub the value of Eqn(4) & Eqn (7) in Eqn. (9) , we get

$$N(E) dE = \frac{\pi}{2} \times \left[\frac{8ma^2}{h^2} \right]^{\frac{1}{2}} \times \left[\frac{8ma^2}{2h^2} \right] dE$$

$$\text{(or)} \quad N(E) dE = \frac{\pi}{2} \times \frac{1}{2} \times \left[\frac{8ma^2}{h^2} \right]^{\frac{3}{2}} \times E^{\frac{1}{2}} dE$$

Pauli's exclusion principle states that 'two electrons of opposite spins can occupy each state'

$$\therefore N(E) dE = 2 \times \frac{\pi}{4} \times \left[\frac{8ma^2}{h^2} \right]^{\frac{3}{2}} \times E^{\frac{1}{2}} dE = \frac{\pi}{2} \times \left[\frac{2 \times 2^2 m}{h^2} \right]^{\frac{3}{2}} \times a^3 \times E^{\frac{1}{2}} dE$$

$$\therefore N(E) dE = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times a^3 \times E^{\frac{1}{2}} dE \quad (10)$$

Density of states is number of energy states per unit volume

$$\therefore Z(E) dE = \frac{N(E)dE}{V} = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times a^3 \times E^{\frac{1}{2}} dE}{a^3}$$

$$\therefore Z(E) dE = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times E^{\frac{1}{2}} dE \quad (11)$$

This is the density of charge carriers in the energy interval 'E' & 'E+dE'.

Carrier Concentration:

Normally all the energy states are not filled. Hence the probability of filling the electron is done by Fermi distribution function (E).

Carrier concentration of electrons in energy bands $n_c = \int Z(E).F(E)dE$

$$(or) n_c = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times E^{\frac{1}{2}} dE.F(E) \quad (12)$$

n_c is known as carrier distribution function

Fermi energy at 0 Kelvin

We know that 0 K maximum energy levels that can occupied by the electron is called Fermi energy level (E_{f_0})

(i.e.,) at 0 K for $E < E_f$ and therefore $F(E) = 1$

\therefore Integrating equation 12 within the limits 0 to E_{f_0} , then the carrier concentration is

$$n_c = \int_0^{E_{f_0}} \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times E^{\frac{1}{2}} dE. = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times \int_0^{E_{f_0}} E^{\frac{1}{2}} dE.$$

$$(or) n_c = \frac{8\pi}{3h^3} (2mE_f)^{\frac{3}{2}} \quad (13)$$

$$(or) E_f = \left(\frac{h^2}{2m} \right) \times \left(\frac{3n_c}{8\pi} \right)^{\frac{2}{3}} \quad (14)$$

This is the Fermi energy of electrons in solids at absolute zero. Thus, Fermi energy of a metal depends only on the density of electrons of that metal.

When the temperature increases .Fermi level(or) Fermi energy slightly decreases

It can be shown that $E_f = E_{f_0} \left[1 - \frac{\pi^2}{12} \left[\frac{kT}{E_{f_0}} \right] \right]$

Importance:

- (i) It is the level which separates the filled valence energy level and vacant conduction energy levels
- (ii) It determines the energy of the particle at any temperature

Average energy of electron s at 0K

$$\text{Average energy of electron } (E_{avg}) = \frac{\text{Total energy of electrons at 0K } (E_T)}{\text{Number of Energy States at 0K } (n_c)} \quad (15)$$

Here, Total Energy of electrons at 0K = Number of Energy states at 0K x Energy of the electron

$$E_T = \int_0^{E_{f_0}} Z(E)dE.E$$

$$\therefore E_T = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \int_0^{E_{f_0}} E^{\frac{1}{2}}.E.dE$$

$$\text{(or) } E_T = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times \frac{E_F^{\frac{5}{2}}}{\frac{5}{2}}$$

$$\text{(or) } E_T = \frac{8\pi}{5h^3} \times (2m)^{\frac{3}{2}} \times E_F^{\frac{5}{2}} \quad (16)$$

Substituting Eqn (13) & (15) in (14), we get

$$E_{Avg} = \frac{\frac{8\pi}{5h^3} \times (2m)^{\frac{3}{2}} \times E_F^{\frac{5}{2}}}{\frac{8\pi}{3h^3} (2m)^{\frac{3}{2}} \times E_F^{\frac{3}{2}}} = \frac{3}{5} E_F^{\frac{5}{2}} - E_F^{\frac{3}{2}}$$

∴ The average energy of electron at 0K is $E_{Avg} = \frac{3}{5} E_{f_0}$

Electron Effective mass

*Effective mass of an electron is the mass of the electron when it is accelerated in a periodic potential and is denoted by m^**

When an electron of mass m is placed in a periodic potential and if it is accelerated with the help of an electric or magnetic field, then the mass of the electron is not constant, rather it varies with respect to the field applied. That varying mass is called as *effective mass* (m^*)

To study the effect of electric field on the motion of an electron in one dimensional periodic potential, let us consider the Brillouin zone which contains only one electron of charge e in the state k , placed in an external field 'E'. Due to the field applied the electrons gains a group velocity quantum mechanically and therefore the acceleration changes.

The group velocity with which the electron can travel is $V_g = \frac{d\omega}{dk}$ (1)

Where $k \rightarrow$ wave vector; $\omega \rightarrow$ angular velocity of electron $\omega = 2\pi\nu$ (or) $\omega = \frac{2\pi E}{h}$ (2)

Substituting equation (2) in equation (1) we get

Group velocity $V_g = \frac{2\pi}{h} \times \frac{dE}{dk}$ (or) $V_g = \frac{1}{\hbar} \times \frac{dE}{dk}$ (3)

If the electron moving in a crystal lattice with momentum P , then the wavelength associated is

$$\lambda = \frac{h}{p} \text{ (or) } p = \frac{2\pi}{\lambda} \times \frac{h}{2\pi} \text{ (or) } P = \hbar k \quad (4)$$

Differentiating equation (4) w.r.t to t $\frac{dP}{dt} = \hbar \frac{dk}{dt}$ (5)

(or) $F = \hbar \frac{dk}{dt}$ (or) $\frac{F}{\hbar} = \frac{dk}{dt}$ (6)

we know acceleration $a = \frac{dV_s}{dt} = \frac{d}{dt} \left[\frac{1}{\hbar} \times \frac{dE}{dk} \right]$

$$= \frac{1}{\hbar} \frac{d^2E}{dk^2} \times \frac{dk}{dt} \quad (7)$$

Substituting equation (6) in equation (7), we get

$$a_s = \frac{1}{\hbar} \frac{d^2E}{dk^2} \times \frac{F}{\hbar} \text{ (or) } a_s = \frac{1}{\hbar^2} \frac{d^2E}{dk^2} F \text{ (or) } F = \frac{\hbar^2}{d^2E / dk^2} a_s \quad (8)$$

Equation (8) resembles with newton's force equation

i.e., $F = eE = m^* a$ (9)

Where m^* is the effective mass of the electron.

Comparing equation (7) and (8), we can write $m^* = \frac{\hbar^2}{d^2E / dk^2}$ (10)

Equation (10) represents the effective mass of an electron in a periodic potential, which depend

on $\frac{d^2E}{dk^2}$

Special cases:

- (i) If $\frac{d^2E}{dk^2}$ is +ve, then effective mass m^* is also positive
- (ii) If $\frac{d^2E}{dk^2}$ is -ve, then effective mass m^* is also negative
- (iii) If $\frac{d^2E}{dk^2}$ is zero, then effective mass m^* becomes infinity

Negative effective mass (or) concept of hole

To show that the effective mass has negative value. Let us take the Energy - wave vector ($E-k$) of a single electron in a periodic potential. i.e., consider the 1st Brillouin zone (allowed energy band) alone as shown in figure.

In the $E - k$ curve, the band can be divided in to two bands viz. upper band and lower band with respect to a point (P) called a **Point of inflection**.

(i) In the **lower band** the value of $\frac{d^2E}{dk^2}$ is a decreasing function from the point of inflection

$\therefore \frac{d^2E}{dk^2}$ is +ve and hence m^* should be +ve in the lower band. If a plot is made between m^* and

k for different values of $\frac{d^2E}{dk^2}$, we get the curve as shown in figure

(ii) In the **Upper band** of $E - k$ the value of $\frac{d^2E}{dk^2}$ is a increasing function from the point of inflection

$\therefore \frac{d^2E}{dk^2}$ is -ve and hence m^* should be -ve in the upper band. If a plot is made between m^* and k

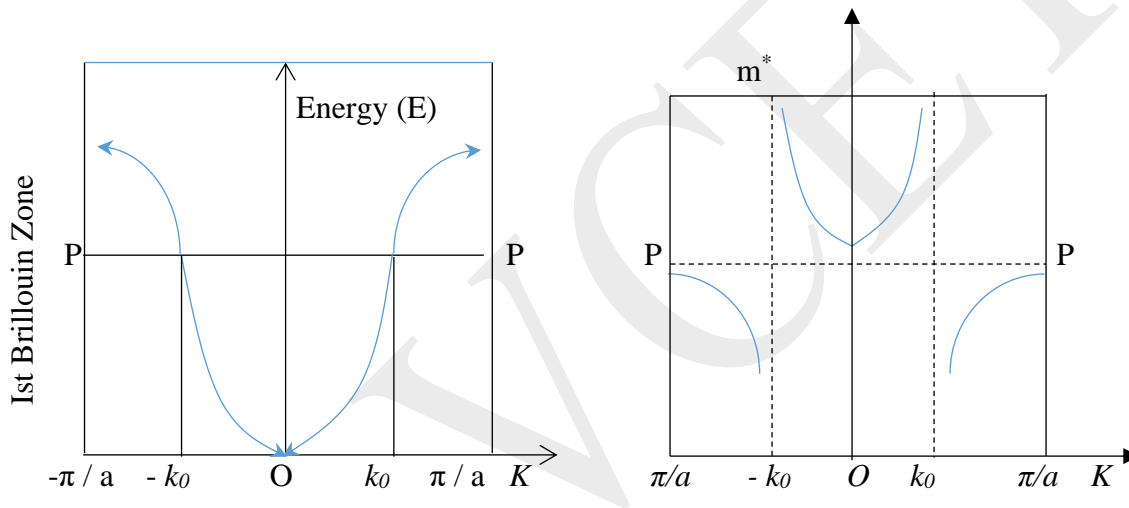
for different values of $\frac{d^2E}{dk^2}$, we get the curve as shown in figure

(iii) **At the point of inflection**, the value of $\frac{d^2E}{dk^2} = 0$ and hence in $m^* - k$ plot, effective mass goes to infinity.

The electron with the negative effective mass is called **Hole**, in other words the electron in the upper band which behaves as a positively charged particle is called hole. It has the same mass as that of an electron but with positive charge.

Therefore, the advantage of the concept of hole is, for a nearly filled band with n number of empty states as shown in figure n number of holes arises

In other words, we can say that the presence of hole is attributed to an empty state, for an electron to be filled. Thus, based on the hole concept several phenomena like Thompson effect, Hall effect, etc., are well explained.



Suggested part – A questions

1. Define Electrical Conductivity?

The amount of electric charge (Q) conducted per unit time (t) across unit area (A) of the solid per unit applied electrical field (E).

$$\sigma = \frac{q}{tAE}$$

2. What are the merits of classical free electron theory?

- (i) It is used to verify Ohm's law
- (ii) It is used to explain electrical and thermal conductivities of metals
- (iii) It is used to derive Wiedemann – Franz law
- (iv) It is used to explain the optical properties of metal.

3. What are the drawbacks of the classical free electron theory?

- Classical theory states that all free electrons will absorb the supplied energy. But quantum theory will absorb certain amount of supplied energy
- Electrical conductivity of semiconductors and insulators could not be explained by this theory
- The phenomenon such as photo – electric effect, Compton effect and black body radiation could not be explained by this theory

4. Define Mean free path?

The average distance travelled by a free electron between any two successive collisions in the presence of an applied field is known as mean free path

$$\lambda = v_d \times \tau_c$$

5. Define collision time?

The average time taken by a free electron between two successive collisions of the electrons is known as collision time

6. Define relaxation time of an electron?

The average time taken by a free electron to reach its equilibrium position from the distributed position due to application of an external electric field is called relaxation time.

7. Define Drift velocity?

The velocity acquired by the free electron due to the application of electric field in the direction opposite to the direction of electric field.

8. Define mobility of electrons?

The magnitude of the drift velocity per unit electric field is defined as the mobility of the electrons

$$\mu = \frac{v_d}{E} \quad \text{unit: mV}^{-1} \text{ S}^{-1}$$

9. State Wiedemann – Franz law? Give the Lorentz number and its value?

“The ratio of electrical conductivity (K) to the thermal conductivity (σ) is directly proportional to absolute temperature (T). i.e., $\frac{K}{\sigma} \propto T$ (or) $\frac{K}{\sigma} = LT$ ”

Where L is the Lorentz number and experimentally, $L = 2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$ at $T = 273\text{K}$

10. What are the sources of the resistance in the metals?

Impurities (ii) Temperature (iii) Number of free electrons

11. Define Fermi energy and Fermi level with its importance?

Fermi Level is the state at which the probability of electron occupation is 50% at any temperature above 0K and also it is the highest reference energy level of a particle at absolute 0K.

Fermi energy is the energy of the state at which the probability of the electron occupation is 50% at any temperature above 0K. It is also the maximum energy of the filled states at 0K.

Importance: Fermi level and Fermi energy determine the probability of an electron occupying a given energy level at given temperature.

12. Define Fermi Distribution Function?

The probability of the electron F (E) occupying at a given energy level at temperature T is known as Fermi Distribution Function. It is given by

$$F(E) = \frac{1}{1 + e^{\frac{E-E_f}{kT}}} \quad \text{Where } E_f \text{ – Fermi Level; } k \text{ – Boltzmann Constant; } T \text{ – Temperature}$$

13. Define density of states. What is its use?

It is defined as the number of available electron states per unit volume in an energy interval E and E+dE. It is denoted by Z(E)

$$\text{i.e., } Z(E) = \frac{\text{No. of available energy states between E and E+dE in a cubical metal piece}}{\text{Volume of that cubical metal piece}}$$

14. What are bound and free electrons?

The electrons which are attached to the atoms and bound to the atomic lattice are called bound electrons. The valence electrons of an atoms free to move throughout the volume of metal like gas molecules of a container are called free electrons.

15. Arrive the microscopic form of Ohm's law? Whether it is true for all temperature?

According to macroscopic theory, Ohm's law is $V = IR$

We know that resistivity is given by $\rho = \frac{RA}{l}$ where R – resistance; A – area of cross section and l is the length of the specimen

$$\therefore V = I \frac{\rho l}{A}$$

$$\text{(or)} \frac{V}{l} = J\rho$$

$$\text{(or)} J = \sigma E \quad [\because E = \frac{V}{l}; J = \frac{I}{A} \text{ \& } \rho = \frac{1}{\sigma}]$$

This is the microscopic form of ohms law and it is not true for all the temperatures.

16. How does electrical resistivity of the metal varies with temperature?

When the temperature is increased, due to increase in thermal vibrations of atoms, the electrons make frequent collisions resulting in reduction of mean free path (λ) and hence resistivity increases.

17. What is meant by degenerate and Non - degenerate state?

For several combination of quantum numbers, if the Eigen value are same with different set of Eigen functions, such states and energy levels are called Degenerate states

For several combination of quantum numbers, if the Eigen value and Eigen functions are same, such states and energy levels are called Non - Degenerate states

18. What is effective mass of electron?

When an electron is accelerated in a periodic potential within the lattice due to external electric or magnetic field, then the mass of the electron varies with respect to the applied field. This varying mass is called effective mass (m^*)

19. Will the effective mass of the electron be negative? Justify your answer?

Yes, the effective mass of the electron can also have a negative value.

Justification: the effective mass of the electron is the mass of the electron when it is accelerated

in a periodic potential and is given by $m^* = \frac{\hbar^2}{d^2E / dk^2}$

Here, $\frac{d^2E}{dk^2}$ can vary from positive to negative value. Therefore if $\frac{d^2E}{dk^2}$ is negative, then m^* will also have negative value. Also, this negative effective mass of an electron leads to the concept of hole.

Physically speaking the electrons with negative mass has same positive mass as that an electron but it has positive charge rather than negative charge

20. Explain the concept of hole and give its importance

When the electrons are accelerated in a periodic potential, its mass varies and it moves in the direction opposite to the direction of the applied field. This variation of mass of an electron is called as negative mass behaviour of electron. The electrons with negative mass is called hole which has same positive mass as that an electron but instead of negative charge, the hole will possess positive charge.

Importance: If we have n number of empty states in a nearly filled band then these n number of empty states can be considered as n number of holes

21. What are the phenomenon that explains the concept of hole?

- (i) Hall effect (ii) Thomson effect

22. What is meant by effective mass approximation?

For an electron moving in a constant potential field $m^* = m$. But for an electron moves in a periodic potential $m^* \neq m$. Thus, when an electron moves in a periodic potential the free electron mass m should be replaced by the effective mass m^* and this process is called as effective mass approximation.

23. What do you understand from Fermi-Dirac statistics and what are fermions?

- (i) The particles are indistinguishable
- (ii) The electrons which obey Fermi-Dirac statistics are called fermions
- (iii) Each energy state can have only one particle with one spin
- (iv) The number of energy states should be greater than or equal to number of particles.
- (v) The total energy of the system = sum of all the energies of the particles.

24. Compare drift velocity and thermal velocity.

Sl.No	Drift velocity	Thermal velocity
1.	It is the average velocity acquired by the free electron in the presence of the electric field	It is the velocity of an electron without any external field
2.	The electrons moving in a direction opposite to the direction of the applied electric field.	The direction of the electrons moving with thermal velocity is random.

Suggested Part-B question

- (i) Based on the postulates of classical free electron, derive an expression for electrical and thermal conductivity of metals and hence arrive Wiedemann-Franz law
- (ii) Write the Fermi-Dirac function. Obtain an expression for the density of states.
- (iii) Obtain an expression for density of states and arrive the allowed energy states per unit volume.
- (iv) Explain the origin of band theory of solids and how the materials are classified as conductors, semiconductors and insulators based on band theory of solids.
- (v) Explain about the theory of tight binding approximation
- (vi) Derive an expression for the effective mass of an electron moving in energy bands of solid. Show how it is vary with wave vector. Arrive the concept of hole